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(54) Title: KETTLE HOP EXTRACTS AND THEIR USE

(57) **Abstract**

A method of making a fully hop flavored beverage employs a hop flavoring agent comprising an extract of hop solids, the hop solids being the residue of a first extraction of hops to remove the alpha acids. Preferably, liquid carbon dioxide is used for the first extraction of the hops and a polar solvent, such as ethanol or water, is used to extract the hop solids. Beverages made by the method and novel compositions for use in the method are also disclosed.

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KETTLE HOP EXTRACTS AND THEIR USE

Technical Field

The present invention generally relates to adding a hop flavor to beverages. More particularly, it relates to a novel method of preparing a fully kettle hop flavored beverage and compositions for use in such method.

Background Art

Hops, in the form of either the ground dried plant or pellets, are used in brewing to give the beverages, such as beer or ale, their characteristic bitter flavor and pleasant aroma. The hops usually are added to the boiling wort in the brewing kettle. Alternatively, if primarily a bitter flavor is desired, a hop extract can be added to the brewing kettle or an isomerized hop extract, if it is highly purified, may be added post kettle, i.e., after the wort has been boiled or after fermentation.

The primary hop constituents which are utilized in the brewing process are the alpha acids, the beta acids, the uncharacterized resins and the hop oils. The alpha

acids are known as humulones and the beta acids are known as lupulones. The alpha acids are the precursors of the bitter substances in beer. The beta acids or lupulones have low solubility in wort and beer and they are believed to play a relatively minor role in the brewing process.

During brewing, chemical changes are made in the alpha acids or humulones resulting in the formation of compounds known as iso-alpha acids, i.e., isohumulone, isocohumulone and isoadhumulone. The alpha acids are extracted from the hops by the boiling wort and isomerized to the iso-alpha acids during the kettle boiling stage.

It is known that iso-alpha acids derived from hops or an unreduced hop extract which contains the iso-alpha acids can cause light instability in malt beverages. The exposure of such a beer or ale to light can result in the beverage becoming "light struck" and having a skunky odor. As a result, such beverages cannot be packaged in clear or green glass bottles without a risk of developing the "light struck" character.

Hop extracts have been used in brewing beer for a number of years. The reasons are severalfold. When whole hops are added to the kettle, the yield of iso-alpha acids is poor, e.g., 10-25% based on the alpha acids present in the hops. However, the conversion of alpha acids in a hop extract to iso-alpha acids can be very high, e.g. 80%. Furthermore, the utilization of the pure iso-alpha acids in a preisomerized extract which is added post kettle is known to be extremely high, e.g. 70-90%.

The predominant production of hop extracts consists of extracting the essential bittering acids from the cellulosic material of the hop blossom by the use of either organic solvents or carbon dioxide. The hops from which the alpha acids have been removed are generally referred to as "spent hops" (but hereinafter referred to

as "hop solids") and they are discarded or sold as animal feed.

The hop extracts thus obtained can be added to the brewing kettle or chemically processed to isomerize and reduce the alpha acids. One disadvantage of the use of hop extracts is that not all the flavor components of the whole hops are completely extracted from the hops and the beverages which have been prepared using hop extracts do not have the "full" hop flavor of beverages made with whole hops.

A number of disadvantages to using hop extracts are noted. For example, the use of a CO_2 or hexane hop extract does not produce a light stable or fully kettle hopped beverage. Also, use of a processed CO_2 hop extract (to make "hydrohop") does not produce a fully kettle hopped beverage. However, it has been surprisingly discovered that the use of hop solids or an extract of hop solids produces a light stable, fully kettle hopped beverage.

Parent U.S. Patent Application Serial No. 08/218,559 advantageously discloses a method of preparing a full hop flavored beverage using the hop solids which have historically been a by-product by the hop extraction process. It has now been surprisingly discovered that an extract of the hop solids itself can be used to produce a beer judged to have a superior hop flavor.

Disclosure Of The Invention

It is the primary object of the present invention to disclose a method of preparing a fully kettle hop flavored beverage.

It is a further object to disclose a method for preparing a fully kettle hop flavored beverage using an extract of the hop. The hop solids have in the past been a discarded by-product of a first hop extraction process.

It is a still further object to disclose novel beverages prepared by the method of the present invention.

It is a further object to disclose novel flavoring agents which comprise an extract of hop solids.

The method of the present invention for making a fully kettle hop flavored beverage comprises adding to a fermentable growth media, prior to bio-conversion, (e.g., prior to or during kettle boil, or post knock out) a hop flavoring agent; and bio-converting the media to form a hop flavored beverage, wherein the hop flavoring agent comprises an extract of hop solids, the hop solids being the residue of a first extraction of hops to remove substantially all the alpha acids, beta acids, and hop oils.

Another aspect of the present invention provides a hop flavored beverage prepared by the foregoing method. A further aspect provides a hop flavored beverage prepared by adding to a fermentable growth media, prior to bio-conversion, a hop flavoring agent comprising an extract of hop solids, the hop solids being the residue of first extraction of hops to remove the alpha acids, beta acids, and hop oils and then bio-converting the media to the hop flavored beverage.

Another aspect of the present invention provides a hop flavoring agent for beverages comprising an extract of hop solids, the hop solids being the residue of a first extraction of hops to remove the alpha acids. Preferably, a non-polar solvent like carbon dioxide or hexane is used for the first extraction of hops. The extraction of the hop solids is preferably accomplished by using a polar solvent.

The polar solvent can be selected from the group consisting of water, ethanol, isopropanol, methanol, dichloromethane, trichloromethane, n-butanol, ethylacetate, ethylene dichloride, and trichlcroethylene. Most preferably the polar solvent is ethanol cr water.

A further aspect of the present invention provides a method of making a fully kettle hop flavored beverage comprising bio-converting a fermentable growth media and adding to the converted media a hop flavoring agent comprising a fermented water extract of hop solids, the hop solids being the residue of a first extraction of hops to remove substantially all the alpha acids, beta acids, and hop oils. A hop flavored beverage is also provided by this method.

A still further aspect of the present invention provides a hop flavored beverage prepared by adding to a bio-converted fermentable growth media a hop flavoring agent comprising a fermented water extract of hop solids, the hop solids being the residue of a first extraction of hops to remove substantially all the alpha acids, beta acids, and hop oils.

A final aspect of the present invention provides a hop flavoring agent for beverages comprising a fermented water extract of hop solids, the hop solids being the residue of a first extraction of hops to remove substantially all the alpha acids, beta acids, and hop oils.

Important advantages of the present invention are that it makes possible the preparation of a fully kettle hop flavored beverage which was previously unavailable and that such a beverage can be prepared using a byproduct of hop solids which is itself an inexpensive and previously discarded byproduct.

A surprising aspect of the present invention is that an extract of the hop solids, in which most of the alpha acids have been removed, can be used in a method of adding a bitter flavor to beverages.

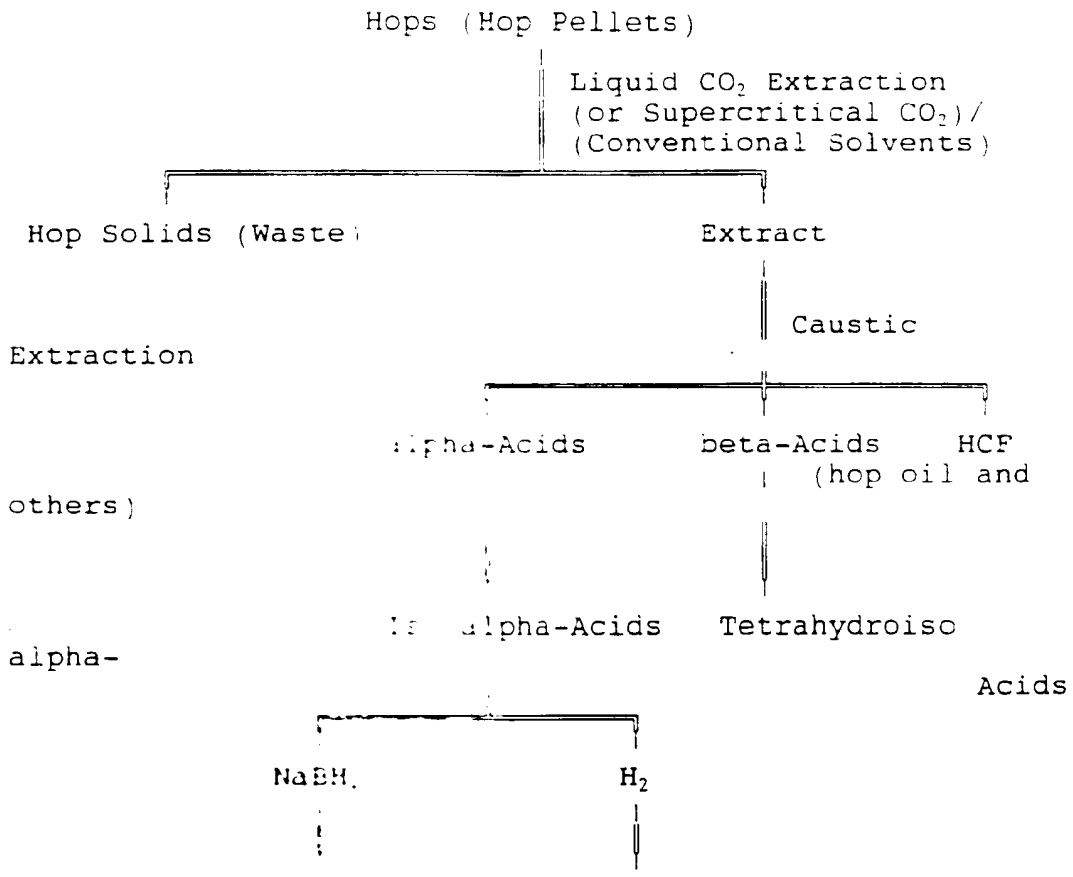
Best Modes For Carrying Out The Invention

Hop solids are those which remain after a hop extract containing substantially all of the alpha acids,

beta acids, and hop oils has been removed from hops, preferably by the liquid carbon dioxide (CO_2) extraction of ground hops or hop pellets. The hop solids are then added in an effective amount to a wort in a brewing kettle prior to or during the boiling of the wort. The wort is then fermented. If additional bittering is desired, a source of isomerized and reduced alpha acids is added before or after fermenting to obtain a light stable beverage with a full hop flavor.

To determine the scope and effectiveness of the present invention experimental work was performed using a CO_2 extract, hop solids, α-acids, β-acids, and HCF prepared from Cascade hop pellets. Supercritical CO_2, ethanol, and caustic extracts were also evaluated. Each fraction was evaluated for its contribution to kettle hop flavor. As a result, it was found that the hop solids effectively imparts a conventional full hop flavor to beer. The results of sensory evaluation confirmed that beverages made with hop solids had a hop flavor similar to that of beverages made using hop pellets. The tests also confirmed that the beer made with the hop solids could be packaged in the clear white (flint glass) or green bottles.

By hop solids we mean the hops which remain after substantially all of the alpha acids, beta acids, and hop oils have been extracted (in whole or in part) from whole hops with a fluid, such as liquid carbon dioxide, supercritical carbon dioxide, hexane, or the like. Generally, hop solids can be the residue remaining after any extraction of hops to remove substantially all of the alpha acids, beta acids, and/or hop oil. The hop solids, alpha-acids and Hop Character Fraction (HCF) can be obtained from whole hops by a process that can be illustrated as follows:



The following is a brief description of the experimental tests performed and the materials employed.

Example 1

Brews were made in a pilot plant with the hop variations as shown in Table 1. All hopping materials were added to the boiling brewery wort 45 min. before the completion of the boil (knock-out). The amounts to be added were calculated based on the bitterness values (BU) of alpha acids that were obtained. The amounts of the material that do not contain alpha acids were added in amounts roughly equivalent to the amounts of alpha acids originally in the pellets.

Table 1. Descriptions and BU Results of Pilot Plant Brewed Beers

Pilot. Brew No.	Hopping Material	Addition Rate	BU (Primary)	BU (Diluted)
1	Pellets	1200mg/L	40.1	30.2
2	LCO_2 Extract	200mg/L	27.1	19.4
3	SuperCO_2 Extract	200mg/L	14.3	9.6
4	β-Rich Fraction	166mg/L	5.7	4.2
5	HCF	166mg/L	3.0	2.2
6	Hop Solids	1200mg/L	15	10.5
7	Caustic Extract	1200mg/L	3.9	2.8

* The diluted beer means the primary beer was diluted with diluent to 6.5% w/w alcohol.

* Pilot Brews 3 to 7 had insufficient bitterness and as a result were spiked with a light stable hop extract to achieve sensorially 20 BU.

These experiments with supercritical CO_2 extract (Pilot Brew No. 3) and caustic extract (Pilot Brew No. 7) were not successful due to insufficient quantities and α-acids contents, but their effects on the kettle hop flavors in the beer were explored.

Three sensory evaluations were performed on the Pilot Brews by a taste panel. Results are summarized below.

1. A QDA method was used for all special samples (No. 2 to No. 6) against the control (pellet hopped No. 1). The QDA procedure is described in detail in McCredy, J.M. et al, Food Technology, 28, 36-41 (1974). Sensory results indicated that the control had significantly stronger kettle hop flavors than the other brews. One possible explanation is that the flavor strength of the individual fraction in the specials (No. 2 to No. 6) is unequal to the whole hop pellets. It is worth noting that the 30 BU value for No. 1 was much greater than all the specials.
2. An alternative QDA paired comparison was performed; each special sample was tasted versus a beer produced

with no kettle hopping (NKH). Results in four categories are summarized in Table 2.

Table 2. Sensory Results Pilot Brews vs. Control in Level of Significance

Pilot Brew	Description	Aroma Strength	Fruity/ Estery	Hop Character	Aftertaste
No. 2	CO_2 Extract	NSD	95.0%	NSD	99.0%
No. 4	β-Rich Fraction	NSD	99.9%	99.0%	95.0%
No. 5	HCF	99.9%	99.9%	99.9%	99.9%
No. 6	Hop Solids	99.9%	99.9%	99.9%	95.0%

Interestingly, of the four attributes tested the panel perceived significant differences in fruity/estery, hop character, and aftertaste in Pilot Brew No. 5 (with HCF) and Pilot Brew No. 6 (with Hop solids).

3. An eight member round table panel was asked to describe the differences between the three samples (Nos. 2, 5, and 6). The panel found that the Pilot Brew No. 6 (with Hop solids) had kettle hop flavors. It was described as having a moderate hop aroma and hoppy taste. The Pilot Brew No. 5 (with HCF) was described as having a green hop/hop oil aroma. While Pilot Brew No. 2 (with CO_2 extract) was found to have a low hop aroma and a moderate hoppy taste.

The test results indicate that hop solids, a waste material from extraction of hops, can be used to impart the kettle hop flavor to beer. Sensory results (both QDA and round table methods) demonstrated that beers brewed with Cascade hop solids (Pilot Brew No. 6) had a moderate level of kettle hop flavors. The beer brewed with HCF had the most hop aroma but not kettle hop aroma. Application of hop solids alone or blended with a specific variety of HCF produces a specific kettle hop flavor similar to that produced by hop pellets added in the kettle. Since hop solids and HCF do not contain alpha acids, beers brewed with these materials can be

prepared and packaged in the clear white or green bottles.

Additionally, the sample brewed with hop solids had 10.5 BU of non-iso-α-acids measured by UV (normal BU method). HPLC analysis of the beer indicated that there were no iso-α-acids present and the BU values were contributed by non-iso-α-acids. These values are significant and greater than the expected background of 2-3 BU. The BU values of beer brewed with liquid CO_2 extract (Pilot Brew No. 2) or α-acids gave a true BU value (of iso-α-acids).

Example 2

Hop Flavors and Light Stability of Pilot Beers Brewed with Reconstructed Hop Pellets

Five types of reconstructed hop pellets were prepared by blending hop solids with water and various fractions of a CO_2 hop extract and forming the mixture into pellets using a pelletizer.

1. Hop solids + CO_2 extract
2. Hop solids + α-acids
3. Hop solids + β-acids
4. Hop solids + HSF
5. Hop solids

The Pilot Brew No. in Table 3 were prepared using the procedure described in Example 1.

Table 3

Pilot Brew No.	Addition Rate of Reconstructed Hop Pellets to Brewery Wort	BU (Primary)	BU (Diluted)
8	Hop Solids (2.25 g/L) + CO_2 Extract (0.4 g/L)	38.6	28.7
9	Hop Solids (2.25 g/L) + α-Acids (0.175 g/L)	30.2	21.3
10	Hop Solids (2.25 g/L) + HCF (0.065 g/L)	12.8	8.9
11	Hop Solids (2.25 g/L)	11.3	8.0
12	Hop Solids (2.25 g/L) + β-Acids (0.248 g/L)	15.0	10.7
13	Hop Pellets (1.5 g/L)	31.2	22.1

All the beers were targeted for 20 BU. As a result, some beers with insufficient BU were spiked with light stable hop extract to achieve sensorially 20 BU. The diluted beer was the primary beer diluted with diluent water to 3.65% w/w of alcohol level. The CO_2 extract was a hop extract made by liquid CO_2 extraction which contained 39.56% α-acids and 44.11% β-acids.

Hop Flavor Evaluation

Pilot Brews 8 through 12 were each evaluated with the control pilot brew (No. 13) and a beer produced with no kettle hopping (NKH). Each evaluation involved monadic sequential testing using the QDA method. Samples were rated on aroma strength, fruity/estery character, hop character and bitterness. The results are shown in Tables 4 to 8. The following significant differences were found:

(a) Cascade Hop solids + CO_2 Extract (Pilot Brew No. 8) had more hop character than the control (No. 13). It also had more aroma strength, fruity/estery character, hop character and bitterness than the NKH beer.

(b) Cascade Hop Solids + Alpha Acids (Pilot Brew No. 9) was not significantly different in the four attributes than the control beer (No. 13).

Pilot Brew No. 9 had more aroma strength, fruity/estery character, hop character and bitterness than the NKH beer.

(c) Cascade Hop Solids + HCF (Pilot Brew No. 10) was not significantly different in the four attributes than the control beer (No. 13). Pilot Brew No. 10 had more aroma strength, fruity/estery character and hop character than the NKH beer.

(d) Cascade Hop Solids Only (Pilot Brew No. 11) was not significantly different in the four attributes than the control beer (No. 13). Pilot Brew No. 11 had more aroma strength, fruity/estery character and hop character than the NKH beer.

(e) Cascade Hop Solids + Beta Acids (Pilot Brew No. 12) had more hop character than the control beer (No. 13). Pilot Brew No. 12 had more aroma strength, fruity/estery character and hop character than the NKH beer.

Table 4

	Mean*				
Characteristic	P.B.No.8	P.B.No.13	NKH	F-Value	Level of Significance
Aroma Strength	15.4^{a}	13.6^{ab}	12.7^{b}	3.52	95.0%
Fruity/Estery	12.8^{a}	11.1^{a}	8.4^{b}	9.12	99.9%
Hop Character	14.0^{a}	11.1^{b}	7.2^{c}	16.47	99.9%
Bitterness	13.3^{a}	13.3^{a}	10.6^{b}	4.68	95.0%
N = 20					
Comments: P.B. No. 8 - grapefruit - 3 panelists					
* Mean scores sharing a common letter are not significantly different at the 95% level.					

Table 5

	Mean*				
Characteristic	P.B.No.9	P.B.No.13	NKH	F-Value	Level of Significance
Aroma Strength	13.3[a]	12.7[ab]	11.6[b]	4.27	95.0%
Fruity/Estery	11.2[a]	10.5[a]	8.3[b]	8.81	99.9%
Hop Character	11.2[a]	11.1[a]	8.6[b]	6.73	99.9%
Bitterness	13.0[a]	12.9[a]	10.6[b]	7.18	99.9%
N = 37					
Comments: P.B. No. 9 - grapefruit - 2 panelists					
* Mean scores sharing a common letter are not significantly different at the 95% level.					

Table 6

	Mean*				
Characteristic	P.B.No.10	P.B.No.13	NKH	F-Value	Level of Significance
Aroma Strength	12.8[a]	11.9[ab]	10.9[b]	3.02	95.0%
Fruity/Estery	10.6[a]	9.5[a]	7.3[b]	7.77	99.9%
Hop Character	11.3[a]	10.6[a]	8.0[b]	7.89	99.9%
Bitterness	11.2[ab]	12.8[a]	10.2[b]	4.30	95.0%
N = 25					
Comments: P.B. No. 10 - grapefruit/citrus - 5 panelists					
* Mean scores sharing a common letter are not significantly different at the 95% level.					

Table 7

Mean*					
Characteristic	P.B.No.11	P.B.No.13	NKH	F-Value	Level of Significance
Aroma Strength	13.4^{a}	12.9^{ab}	11.8^{b}	3.68	95.0%
Fruity/Estery	12.2^{a}	11.0^{a}	8.0^{b}	10.51	99.9%
Hop Character	11.0^{a}	10.5^{a}	8.2^{b}	5.31	99.0%
Bitterness	11.3^{ab}	12.5^{a}	10.5^{b}	3.05	95.0%
N = 25					
Comments: P.B. No. 11 - grapefruit/citrus - 6 panelists P.B. No. 13 - green hop/dry hop - 2 panelists					
* Mean scores sharing a common letter are not significantly different at the 95% level.					

Table 8

Mean*					
Characteristic	P.B.No.12	P.B.No.13	NKH	F-Value	Level of Significance
Aroma Strength	13.8^{a}	12.2^{ab}	11.8^{b}	3.72	95.0%
Fruity/Estery	11.1^{a}	9.6^{ab}	8.2^{b}	3.64	95.0%
Hop Character	12.5^{a}	9.9^{b}	8.9^{b}	7.08	99.0%
Bitterness	11.3^{ab}	12.3^{a}	10.3^{b}	3.19	95.0%
N = 20					
* Mean scores sharing a common letter are not significantly different at the 95% level.					

The Pilot Brews No. 10, No. 11 and No. 13 also were evaluated against a control which was a beer produced with no kettle hopping (NKH) by a round table panel.

An eight member round table panel were asked to describe the differences in hop aroma and hop flavor. The results are reported in Table 9.

The panel found the control to have the least aroma, low hop aroma and low bitterness. The pilot brew formulated with Cascade hop solids and HCF (Pilot Brew

No. 10) was found to have the most aroma and hop aroma. It was described as the fruitiest of the four products with a pineapple/grapefruit character and a moderate bitterness. The pilot brew formulated with Cascade hop solids (P.B. No. 11) and the pilot brew formulated with Cascade hop pellets (P.B. No. 13) both had a grapefruit/citrus character, a moderate hop character and a moderately strong bitterness. They both were perceived as being more bitter than P.B. No. 10 and the control.

Table 9

Round Table Results

Hop Characteristics	Control	Hop Solids + HCF P.B. No. 10	Hop Solids P.B. No. 11	Hop Pellets P.B. No. 13
Aroma	least aroma	most aroma		
		most fruity		
		pineapple/grapefruit	grapefruit/ citrus	grapefruit/ citrus
	low hop aroma	most hop aroma	moderate hop aroma	moderate hop aroma
Flavor	low bitterness	moderate bitterness	moderately strong bitterness	moderately strong bitterness

Light Stability Evaluation

A 10-day light stability test on the above beers was conducted by a taste panel (6 people). The samples packaged in sealed clear bottles were placed in open low-side six pack carriers and set under 25 foot-candles of fluorescent light. At the end of a 10-day period, the samples were evaluated for the degree of light struck character, which is evidenced by the presence of a skunky odor.

Pilot Brew Nos. 10 and 11 did not produce the light struck character while Pilot Brew Nos. 8, 9, and 13 produced significant amounts of light struck character. However, Pilot Brew No. 12 gave a slight light struck

character. It might be due to residual amounts of alpha acids present in the beta acids.

Description Of The Preferred Embodiments

By a fermentable growth media we mean (1) a conventional wort, or (2) any minimal media containing Difco yeast N base (.8 - 8g/l, preferably 1.7 g/l) and glucose (1 - 20% by weight, preferably 8 - 10%), or any combination of (1) and (2). By bio-converting we mean a fermentation process whereby hop solids extract is converted to kettle hop flavor wherein glucose is present and the yeast is at a fermentable temperature.

1. Ethanol Extract of Hop Solids

Example 3

The further aspect of the present invention of using an extract of hop solids (the hop solids being the residue of a first extraction of hops to remove the alpha acids) to make a hop flavored beverage results in a beverage which is rich in positive hop components (fruity, estery, hoppy) and devoid of negative ones (dry hop, green, tea-like, hop oil-like). Various components of cascade hops (whole pellet; CO_2 extract; HCF fraction of CO_2 extract) were investigated to evaluate their capacity to deliver kettle hop flavor to a finished brew.

Sensory panels concluded that no significant level of kettle hop flavor was associated with any CO_2 extract or fraction thereof. This lead to the conclusion that the component responsible for kettle hop flavor must still reside in the spent (CO_2 extracted) hop. Using the CO_2 extracted hop solids to make a hop flavored beverage confirmed that it indeed contained the precursor material which is converted during fermentation into "kettle hop flavor". See Example 1 and Table 2, supra.

CO_2 extracted hop solids is typically in the form of dust which makes it difficult to handle. One option

explored was solvent extracting the dust so that the important hop flavor components could be delivered as an easily handled liquid. Thus, ethanol was employed as a solvent to extract spent Cascade and spent Galena hop solids.

Referring now to Table 10, several 10 gallon lab brews were made using the ethanol extract from hop solids and the brews were then evaluated. A pale malt beverage product with the special ethanol extract (PPI-03-112894) was submitted for sensory testing (colum 2). The product was monadically evaluated by fifteen panelists who routinely evaluate interplant beverage samples. Nine flavor attributes were rated in replicate using the QDA method. Mean scores are based on a 24-point linear scale.

The results are given below. Compared to a low hop flavored pale malt beverage (column 3), this product has more aroma strength, fruity/estery character, hop character, diacetyl character and aftertaste than typically found for a low hop flavor pale lager beverage.

Table 10

Characteristic	Ethanol Extract Flavored Pale Lager Beer (Mean Score)	Low Hop Flavor Pale Lager Beer (Mean Score)
Aroma Strength	14.0	11.8
Fruity/Estery	11.8	9.2
Hop Character	10.4	8.5
Malty/Grainy	7.8	N/A
Sulphidic/tic	5.7	5.3
Diacetyl	4.8	3.7
Bitterness	11.0	10.6
Body	11.3	N/A
Aftertaste	12.0	10.8
Comments: fruity/estery - 3 panelists		

The evaluation showed that a most pleasant estery hop flavor was produced using the ethanol extract and was judged more pleasurable than using hop solids alone. This lead to the understanding that ethanol extraction removes the most pleasant attributes from hop solids, but not the negative ones.

This observation was confirmed by evaluating brews made with (1) hop solids; (2) ethanol extracted hop solids; and (3) ethanol extract of hop solids. The brew with hop solids (1) had a typical cascade kettle hop flavor. The brew with ethanol extracted hop solids (2) had a distinct dry hop flavor lacking in fruity, estery attributes. The brew with the ethanol extract of hop solids (3) had an unusually pleasant fruity/estery/hoppy flavor and aroma which is prized in hop flavored beverages (see Table 10). By dry hop flavor we mean any flavor derived from adding hops post-fermentation.

Although ethanol is the most preferred solvent for extracting hop solids, it is envisioned that any polar solvent will work. We envision the preferred extraction solvents to include water, isopropanol, methanol, dichloromethane, trichloromethane, n-butanol, ethyl acetate, ethylene dichloride, and trichloroethylene.

The amount of hop solids extract to be added depends upon the amount of flavoring desired in the resulting beverage and the concentration of the desired extract components in the extraction solvent. Typically, the amount of hop solids extract added will range from 10 ppm to 10,000 ppm, more preferably 100 ppm to 5,000 ppm, and most preferably from 1,000 ppm to 3,000 ppm (based on the extraction of a given amount of hop solids).

CO_2 extraction of Cascade hops. The hops were extracted with liquid CO_2 at 50°F and 700 psi. The residue (the hop solids) was retained for further processing.

Preparation of an ethanol extract of hop solids. A sample of Cascade hop solids was obtained from the hop

pilot plant liquid CO_2 extractor, runs 640-641. The hop solids were greatly depleted of alpha acids (only 0.3% left), beta acids, and hop oils. The hop solids are normally treated as a waste fraction, considered as having no value. Normally only the CO_2 extract is considered as having value.

110.9 grams of hop solids were slurried with 576 grams of 95% v/v ethanol and poured into a glass chromatography column. The ethanol was allowed to slowly percolate at ambient temperature and pressure through the bed of hop solids. The filtered eluate (dark green colored ethanol extract) was collected (yield 350.6 grams wet weight).

Preparation of beer kettle hopped with the ethanol extract. A sample of Milwaukee Brewery wort from the cooler (which contained a negligible amount of hops products) was brought to the lab for a re-boil. 18.2 kg of cooler wort and 2.0 kg water were brought to a boil in a kettle. 95.9 grams of ethanol extract (1,000 ppm based on hop solids) (see above) were added at 60 minutes before knockout. At 30 minutes before knockout, another 95.9 grams of ethanol extract (1,000 ppm based on hop solids) were added to the kettle. The knockout wort 16.8 kg was cooled and pitched with 12 million yeast cells/ml, aerated and fermented at 60°F for 7 days. The young beer was primary filtered and finished to a 3.65% w/w alcohol. The resulting beer was deemed to have a desirable estery/hoppy flavor, free of dry hop flavor as evaluated by the fifteen member expert round table as shown in Table 10.

2. Water Extract of Hop Solids

Example 4

Water can also be used to obtain an extract of the hop solids which, when added before the fermentation step, produces a desirable hop flavored beverage. The water extract of the hop solids is hereinafter referred

to as "hop tea." Likewise, the hop tea may be fermented and used to produce a desirable hop flavored beverage. The fermented top tea may be used as is, or it may be further processed by ultrafiltration (through a 300 nominal molecular weight cutoff membrane) whereby the permeate may be used as the hop flavoring. Gases from the hop tea fermenter may also be cold-trapped, whereby the condensate may be used as the hop flavoring.

One advantage of using a fermented hop tea (or permeate/condensate) is that it may be added after fermentation to produce a desirable hop flavored beverage. Thus, the fermented hop tea may be added post-fermentation to customize any desired level of hop flavoring to the finished hop flavored beverage.

Referring now to Tables 11, 12 and 13 below, a number of hop flavored beverages were made using the above hop teas and evaluated by a fifteen member sensory panel. Nine flavor attributes were rated in replicate using the QDA method. Mean scores are based on a 24 point linear scale. The control sample was an unhopped pale malt lager beer.

Sample #2 was a hopped beer made with hop solids according to the principles in Examples 1 and 2, above (hop solids added at 3,000 ppm). Samples #7 and #9 are hopped beers made with hop solids at 15,000 ppm but blended with unhopped stock beer for a final 3,000 ppm hop solids equivalent. Samples #3 through #6 are hopped beers made with hop tea (produced by the exhaustive extraction of hop solids with water at either 170° or boiling) added at a 3,000 ppm hop solids equivalent.

Sample #8 is a hopped beer made by adding post-fermentation a fermented hop tea to a 3,000 ppm hop solids equivalent. The hop tea was pitched with 25 x 10^6 cells/ml of standard brewing yeast and was fermented at 60°F for 10 days using minimal media (Difco yeast N base and glucose).

BFKO means "before knock out." SCO_2 means hops extracted with supercritical CO_2. LCO_2 means hops extracted with liquid CO_2. MR means a pale malt lager beer.

Table 11

Sample ID	Description
Control	Control - Unhopped
#2	Standard - Steiner Galena SCO_2 Hop Solids - 3000 ppm 60 min. BFKO
#3	Experimental - Hop Tea added 60 min. BFKO - 3000 ppm equivalent (Steiner Galena SCO_2 Hop Solids extracted with BOILING water - 30,000 ppm)
#4	Experimental - Hop Tea added 60 min. BFKO - 3000 ppm equivalent (Steiner Galena SCO_2 Hop Solids extracted with 170° water - 30,000 ppm)
#5	Experimental - Hop Tea added 0 min. BFKO - 3000 ppm equivalent (Steiner Galena SCO_2 Hop Solids extracted with 170° water - 30,000 ppm)
#6	Experimental - Hop Tea added at Fermentation - 3000 ppm brew kettle equivalent (Steiner Galena SCO_2 Hop Solids extracted with 170° water - 30,000 ppm)
#7	Experimental - Fermented Galena hop solids hopped beer blended post Fermentation - 3000 ppm brew kettle equivalent (Steiner Galena SCO_2 Hop Solids added to MR at 15,000 ppm and fermented - blended 85.3% MR stock)
#8	Experimental - Fermented hop tea added post Fermentation - 3000 ppm brew kettle equivalent (Steiner Cascade SCO_2 Hop Solids extracted with boiling water - 30,000 ppm and diluted to 15,000 ppm with water and mininal medium containing 10% Dextrose final)
#9	Experimental - Fermented Cascade hop solids hopped beer blended post Fermentation - 3000 ppm brew kettle equivalent (Miller Pilot Cascase LCO_2 Hop Solids added to MR at 15,000 ppm and fermented - blended with 85.3% MR stock)

Table 12

ANALYSIS OF VARIANCE									
Mean Score*									
Attribute	Control	#2	#3	#4	#5	#6	#7	F-Value	Level of Significance
Aroma Strength	10.6[b]	11.5[a]	11.1[a]	11.8[a]	11.5[a]	11.7[a]	12.1[a]	2.22	95.3%
Fruity/ Estery	8.3[b]	10.1[a]	9.7[a]	9.7[a]	9.7[a]	9.7[a]	8.7[ab]	3.46	99.7%
Hop Charater	8.4[a]	8.1[a]	8.7[a]	8.8[a]	9.0[a]	8.9[a]	8.2[a]	1.47	NSD
Malty/ Grainy	7.9[a]	7.4[a]	7.6[a]	7.1[a]	7.1[a]	7.5[a]	7.6[a]	0.66	NSD
Sulphidic/ tic	5.0[ab]	4.7[b]	5.4[ab]	5.0[ab]	5.3[ab]	6.0[a]	5.5[ab]	2.24	95.6%
Diacetyl	3.6[b]	4.1[b]	4.5[b]	4.5[b]	4.5[b]	4.0[b]	8.0[a]	9.70	99.9%
Bitterness	9.9[a]	10.2[a]	9.7[a]	10.4[a]	9.7[a]	10.3[a]	10.3[a]	1.53	NSD
Body	10.2[a]	10.4[a]	10.3[a]	10.2[a]	10.2[a]	10.0[a]	10.9[a]	1.52	NSD
Aftertaste	10.1[a]	10.4[a]	10.7[a]	11.0[a]	10.2[a]	10.7[a]	10.9[a]	1.71	NSD
N = 21									

Comments: #2 - fruity - 2 panelists
- winey - 2 panelists
#5 - oxidized - 2 panelists
#6 - oxidized - 3 panelists

*Mean scores sharing a common letter are not significantly different.

Table 13

ANALYSIS OF VARIANCE					
Mean Score*					
Attribute	Control	#8	#9	F-Value	Level of Significance
Aroma Strength	11.0^{c}	13.5^{a}	12.2^{c}	21.48	99.9%
Fruity/Estery	7.9^{b}	9.4^{a}	9.3^{a}	7.75	99.9%
Hop Character	8.2^{b}	8.6^{b}	9.6^{a}	6.96	99.8%
Malty/Grainy	7.2^{b}	7.1^{b}	8.0^{a}	3.85	97.4%
Sulphidic/tic	5.6^{a}	5.6^{a}	5.9^{a}	0.44	NSD
Diacetyl	3.3^{b}	10.4^{a}	4.8^{b}	36.83	99.9%
Bitterness	9.5^{c}	10.6^{b}	12.1^{a}	26.72	99.9%
Body	9.9^{b}	10.7^{a}	11.3^{a}	6.52	99.8%
Aftertaste	9.7^{b}	12.1^{a}	11.9^{a}	12.80	99.9%
N = 39					
Comments: #8 - diacetyl - 8 panelists - spoiled - 4 panelists					
* Mean scores sharing a common letter are not significantly different					

Tables 11 through 13 show that a hop tea or fermented hop tea may be used to produce a hop flavored beverage having a desirable aroma, fruity/estery attributes, and a favorable hop character. Depending on the desired attributes of the finished hop flavored beverage, the hop solids, hop tea, or fermented hop tea can be added at 0.1 to 7.5 lbs/barrel based on hop solids equivalent.

Other considerations. Although the present invention has been described wherein the ethanol extract is added to the kettle boil, it is also possible to add the polar solvent extract post kettle but prior to fermentation.

The preferred percentage depletion of alpha acids, beta acids, or hop oils in the hop solids (compared to the original whole hop material) is >80%, >80%, >80%, respectively. The most preferred ranges are ≥90%, ≥90%, ≥90%, respectively.

The polar extraction solvent also can be a mixture of ethanol and water in any combination.

Conclusions

The foregoing test results indicate that there was essentially no kettle hopped flavor difference between the light stable beer made by the method of the present invention and the light unstable beer made with hops. The beers made by the practice of the present invention had acceptable taste and foam characteristics, as well as light stability due to the low level of iso-alpha acids. Thus, it is possible by the practice of the method of the present invention to prepare a light stable, full hop flavored beer using hop solids and extracts of hop solids.

It will be apparent to those skilled in the art that the method of the present invention, in addition to being novel and useful, is also simple and economical. For example, only conventional brewing techniques and equipment are used and the useful flavoring constituents of the hop solids are not wasted.

The hop solids preferred for use in the method of the present invention are the hop solids obtained after the liquid carbon dioxide extraction of hops under 40° to 80°F and 500 - 1000 psig. The liquid carbon dioxide extraction of hops is described in U.S. Patent No. 4,344,978. Other hop solids that can be used are those obtained by the extraction of hops with supercritical CO_2 at a temperature of 100° - 150°F and pressure of 1100 - 3000 psig., or by the practice of the extraction methods of U.S. Patents Nos. 3,798,332; 4,002,683; and others.

Representative of the different types of hops that can be used to prepare the hop extract and hop solids are Cascade hops and Galena hops. However, other varieties of hops also can be used.

The amount of hop solids extract to be added depends upon the amount of kettle hop flavor desired in the resulting beverage. Normally, if the hop solids extract are used alone the amount employed will be equivalent to the equivalent amount of whole hops that would be employed for the same flavor whole hopped beer. When the preferred composition containing both hop solids and HCF are used the amount employed will be about 0.5x to about 3x or more of the amount of whole hops that would be employed.

It will be apparent to those skilled in the art that a number of modifications and changes may be made without departing from the spirit and scope of the invention.

For example, an exhaustive extraction of hop solids with boiling ethanol resulted in about a 28% by weight extract on a dry basis. Also, an exhaustive extraction of hop solids with boiling water resulted in about a 45% by weight extract on a dry basis. Both of these extracts produce a fully kettle hop flavored beverage.

Therefore it is to be understood that the invention is not to be limited by the description and examples but only by the claims which follow.

Industrial Applicability

The invention is useful for providing a fully kettle hop flavored beverage rich in positive hop components (fruity, estery, hoppy) and devoid of negative ones (dry hop, green, tea-like, hop oil-like).

CLAIMS

We claim:

1. A method of making a hop flavored beverage from a fermentable growth media comprising the steps of:

adding to the media, prior to bio-conversion, a hop flavoring agent; and

bio-converting the media to form the hop flavored beverage, wherein the hop flavoring agent comprises an extract of hop solids, the hop solids being the residue of a first extraction of hops to remove substantially all the alpha acids, beta acids, and hop oils.

2. The method of claim 1, wherein carbon dioxide is used for the first extraction of hops.

3. The method of claim 1, wherein at least one polar solvent is used to extract the hop solids.

4. The method of claim 3, wherein the polar solvent is selected so that it extracts essentially no dry hop flavor components from the hop solids.

5. The method of claim 3, wherein the polar solvent is selected from the group consisting of water, ethanol, isopropanol, methanol, dichloromethane, trichloromethane, n-butanol, ethyl acetate, ethylene dichloride, and trichloroethylene.

6. The method of claim 5, wherein the polar solvent is ethanol.

7. The method of claim 5, wherein the polar solvent is water.

8. A kettle hop flavored beer having enhanced light stability in a clear or green glass bottle which is prepared by the method of claim 1.

9. A hop flavored beverage prepared by the method of claim 1.

10. A hop flavored beverage prepared by the method claim 4.

11. A hop flavored beverage prepared by the method of claim 6.

12. A hop flavored beverage prepared by the method of claim 7.

13. A hop flavored beverage prepared by adding to a fermentable growth media, prior to bio-conversion, a hop flavoring agent comprising an extract of hop solids, the hop solids being the residue of a first extraction of hops to remove substantially all the alpha acids, beta acids, and hop oils, and then bio-converting the media to form the hop flavored beverage.

14. An improvement in the brewing method for making a hop flavored beverage which comprises adding to a fermentable growth media, prior to bio-conversion, a hop flavoring agent comprising an extract of hop solids, the hop solids being the residue of a first extraction of hops to remove substantially all the alpha acids, beta acids, and hop oils.

15. A hop flavoring agent for beverages comprising an extract of hop solids, the hop solids being the residue of a first extraction of hops to remove substantially all the alpha acids, beta acids, and hop oils.

16. The hop flavoring agent of claim 15, wherein the hop flavoring agent comprises a polar solvent extract of hop solids.

17. The method of making a hop flavored beverage from a fermentable growth media comprising steps of:

bio-converting the media; and

adding to the converted media a hop flavoring agent comprising a fermented water extract of hop solids, the hop solids being the residue of a first extraction of hops to remove substantially all the alpha acids, beta acids, and hop oils.

18. A hop flavored beverage prepared by the method of claim 17.

19. A hop flavored beverage prepared by adding to a bio-converted fermentable growth media a hop flavoring agent comprising a fermented water extract of hop solids, the hop solids being the residue of a first extraction of hops to remove substantially all the alpha acids, beta acids, and hop oils.

20. An improvement in the brewing method for making a hop flavored beverage which comprises adding to a bio-converted fermentable growth media a hop flavoring agent comprising a fermented water extract of hop solids, the hop solids being the residue of a first extraction of hops to remove substantially all the alpha acids, beta acids, and hop oils.

21. A hop flavoring agent for beverages comprising a fermented water extract of hop solids, the hop solids being the residue of a first extraction of hops to remove substantially all the alpha acids, beta acids, and hop oils.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/07325

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C12C 3/00, 3/08, 11/00
US CL : 426/ 16, 592, 600
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 426/ 16, 592, 600

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ---- Y	SU, A, 1,601,112 (LEKHOV ET AL) 23 October 1990, pages 1 and 2 of the translation.	1-5, 7-10, 12-16, 18, 21 ---------- 7, 17
X	BE, A, 753,555 (ANH) 31 December 1970, pages 1 and 2 of the translation.	1-4, 8-20
X	GB, A, 6,243 (MEWBURN) 21 May 1885, page 1.	1-4, 8-20
A	Malting and Brewing Science, Volume I Malt and Sweet Wort, 1981, D. E. BRIGGS ET AL., page 6.	

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 10 JULY 1996	Date of mailing of the international search report 02 AUG 1996
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer ESTHER KEPPLINGER Telephone No. (703) 308-2339

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